NASA TT F-10,810

TEMPERATURE DEPENDENCE OF THE GRAIN SIZE IN $NbC_{0.80}$

S. S. Ordan'yan and A. I. Avgustinik

Translation of "O temperaturnoy zavisimosti razmera zeren $NbC_{0,80}$"
Poroshkovaya Metallurgiya,
Vol. 6, No. 9, pp. 50-54, 1966

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 MARCH 1967

TEMPERATURE DEPENDENCE OF THE GRAIN SIZE IN $NbC_{0.80}$

S. S. Ordan'yan and A. I. Avgustinik

ABSTRACT. Study of the temperature dependence of the grain size in nonstoichiometric $NbC_{0.80}$ for temperatures from 1600 to 3300°K in vacuum and argon. The grain growth activation energy is 65.5 kcal/mol, a value that suggests a diffusion grain growth process that takes place on grain boundaries and surfaces.

The carbides of transition metals of Groups IV and V are promising compounds for the production of high-temperature structural materials (ref. 1) and also of materials for the direct conversion of heat into electricity (ref. 2). In both cases the materials, as a rule, are utilized for a period of many hours at temperatures exceeding 2000°. This may lead to significant changes of structure and consequently to changes in some of the alloy properties. In this case, the basic process in homogeneous materials is the increase in grain size due to recrystallization. A large effect on the growth of grains is produced by the change in the chemical composition of the solid phase. /50*

In the use of carbides of metals from Group V (for example, NbC) with a composition at each given temperature which vaporizes without the disruption of the formal ration of components $Me^{V}C_{x}$ (refs. 3-6, 7), the variation in the initial composition is also observed as temperature is changed because according to data (refs. 8 and 9) the interval of temperatures for congruent vaporization in the case of metal carbides of Group V is narrow. This change in composition at high temperatures is usually accompanied by a change in such important parameters as surface tension and diffusion coefficient, which determine the growth of grains, i.e., the operating properties of the alloy are affected.

With the above in mind, when investigating the temperature dependence of grain size of nonstoichiometric niobium carbide in the temperature range 1600-3300°K, we selected a composition inside the region of homogeneity close to the one specified by Fries (ref. 6) which vaporizes congruently at high temperatures. Similar investigations for more complex alloys become difficult because it is necessary to produce a hydro-carbon gaseous medium providing for a constant composition of the solid phase over a wide temperature range.

The initial materials used to synthesize the alloy $NbC_{0.80}$ were powdered niobium containing more than 99.5 percent of the basic component (with Ta, W, Fe, and other impurities) and acetylene soot. The synthesis was carried out at 1800°K for 1.5 hours in the TVV-4 furnace at a vacuum of $1\text{-}3\times10^{-4}$ mm Hg. X-ray examination and chemical analysis confirmed a complete reaction leading to the

*

Numbers in the margin indicate pagination in original foreign text.

formation of imperfect niobium carbide. The pellets were ground until they passed through a sieve with 10,000 meshes/cm^2 and were then placed into a vibratory mill where the powders were pulverized by means of VK-6 alloy balls in an ethyl alcohol agent. The specific surface area measured by the Deryagin method (ref. 10) and $3.3 m^2$/gram. Two types of samples were prepared from the powder: 1) dry-pressed samples 10mm in diameter and of the same height, 2) extruded samples 3mm in diameter with a length of 50mm. The first were used for /51 investigations in the temperature range 1600-2200°K during external heating, while the second were used for 2200-3300°K with a direct passage of an electrical current using a set-up described in reference 11.

The experiments in the temperature range 1600-2200°K were carried out in a vacuum using a TVV-4 furnace; the temperature was raised to the specified value over a period of one hour and the samples were soaked for 0.5 hr at the final temperature. Above 2200°K experiments were carried out in a pure argon atmosphere also with a half hour soaking at the final temperature*. Samples for the high-temperature investigations were sintered initially at 2200°K for a period of 0.5 hr in the TVV-4 furnance and were then soaked at higher temperatures in argon.

After soaking, the samples were subjected to metallographic analysis. Before this, they were polished by conventional methods and the polished sections were etched with a mixture of nitric and fluoric acids. After the grain boundaries were exposed, the number of grains were counted on arbitrary regions of the test samples. We carried out 250 to 400 measurements (ref. 12), and the results of these were used to construct histograms and to determine the average diameter of the grains by means of the equation:

$$d_{av}$$

where d_{av} is the average arithmetical size of the grain; d_i is the size of the grains in each group; m_{d_i} is the number of grains contained in a group; m is the number of measured grains.

Investigations showed that even at a temperature of 1800°K there was an enlargement of grains to 1.52mμ in pellets pressed from particles with an average size of 0.25mμ. Soaking at 2000°K leads to a substantial development of contacts between grains. Basically, the size of the pores is comparable to the size of the grains which average 4-5mμ (fig. 1.a). In the temperature range 2500-2900°K, the substantial growth in grain size is accompanied by a substantial redistribution of the pores: the pores dissolve in the crystals and then are

*

Since the samples in the temperature range 2200-3300°K were heated by passing an ac current through them, the possible effect of the electrical transport of carbon on the results of the experiments was not taken into account.

separated along the grain boundaries (fig. 1,b,c). During the preliminary temperatures, the grain boundaries are basically separated from the pores and approach the equilibrium form (fig. 1, d), and the pores coagulate into cavaties which are greater than the initial ones as well as those which exist after soaking at intermediate temperatures. The average grain size reaches a value of 100mμ.

Since the grain surface (the area of the boundaries), which is subject to the diffusion processes, is proportional to the square of the grain diameter, we constructed the relationship $\ln d^2 = f(\frac{1}{T})$ (fig. 1), which has the following analytical expression:

$$d^2 = 1.78 \cdot 10^8 \exp\left(-\frac{65\,500}{RT}\right)_{t=30}.$$

By using the slope of the straight line (fig. 2), which determines the activation energy for the grain-growth process, we obtained a value for the latter equal to 65.6 kcal/mole. From this relationship we determined the temperature for the beginning of growth in the initial grains at 1610°K.

As we know, the grain growth (ref. 13) is determined by the energy of the separation surface, i.e., by the surface tension of grain boundaries. Usually it is assumed that the energy consumed in the migration of grain boundaries is less in absolute value than the energy of activation for the volumetric self-diffusion and that it is comparable with the activation energy of self-diffusion along the grain boundaries. In materials similar to the one investigated, the activation energy of self-diffusion for the metalloid and metal is different. Taking into account the crystalline peculiarities in the structure of carbides for transition metals from Groups IV and V, particularly the dimensional factors and the possible existence of a large vacancy concentration phases in the C-sublattice, we can assume they affect the activation energy of self-diffusion not only of carbon but also of metallic atoms, as well as on the magnitude of the entropy factor in the equations of self-diffusion for the alloy components. To date there is almost no reliable information on the diffusion constants for high-temperature metal-like compounds. The data presented in reference 14 on the investigation of the diffusion of carbon and niobium in various phases of the system Nd-C apparently must be refined, because the use of highly porous compounds could lead to the recording of some total coefficient of diffusion including both the volumetric and surface atoms for which the activation energy of diffusion is different. /52

The values of activation energy for the self-diffusion of niobium in $NbC_{0.96}$ (55 kcal/mole) obtained by the authors is much less than the value in pure niobium (115 kcal/mole (ref.14)). The reference made by the authors to large intra-atomic distances and a different nature of the matrix is most probably insufficient to explain the values which they observed experimentally, because the lattice expansion takes place together with the establishment of rigid directional bonds Me-C, which strain-harden the lattice of the compounds /53

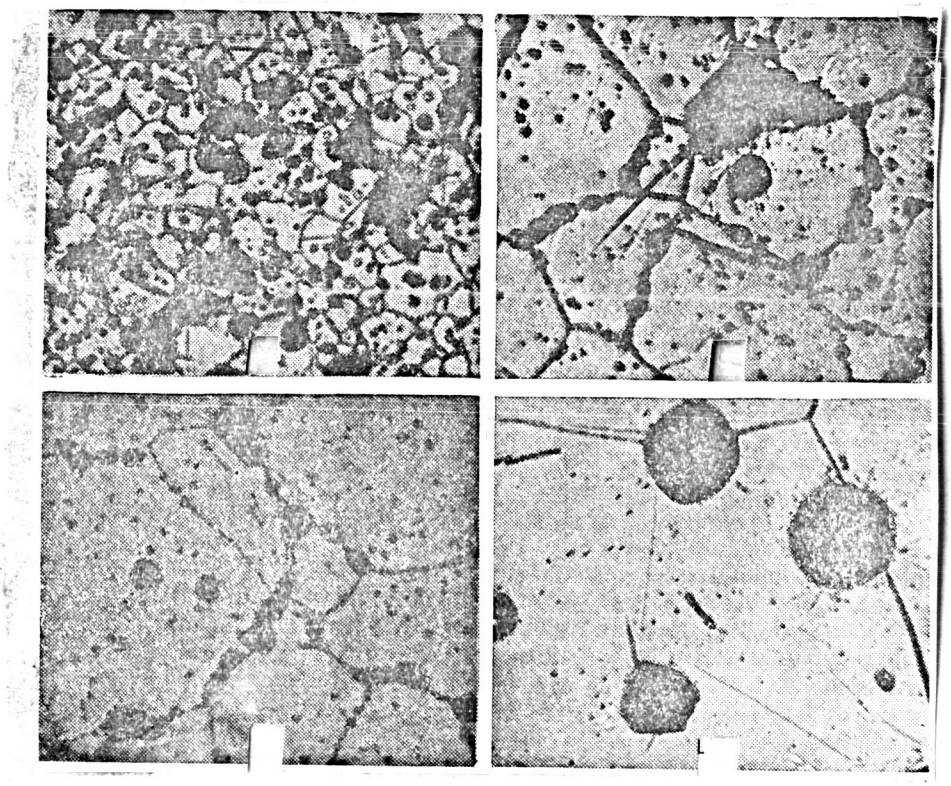

Figure 1. The Structure of the Alloy $NbC_{0.80}$ After 0.5 hours of soaking. X 1000: a-2000°K, b-2570°K, c-2920°K, d-3280°K.

(T_{fus}, the modulus of elasticity, and so forth are increased), which apparently must lead to a substantial increase in the activation energy for the self-diffusion of niobium.

During the growth of grains, in spite of the different diffusion parameters of the components, the composition of grain boundaries does not change, i.e., this process is determined as the slowest one like the diffusion mobility of niobium atoms. Therefore, we must assume that the coincidence of the activation energy for the boundary self-diffusion of niobium (55 kcal/mole) and of the energy for the growth of grains in $NbC_{0.80}$ (65 kcal/mole) is satisfactory. On the data which have been obtained, taking into account the existing relationship between $U_{boundary}$ and U_{volume}, we may assume that the activation energy for the self-diffusion of niobium in NbC_x and of the processes controlled by the mobility of niobium atoms, will be of the order of 120-140 kcal/mole.

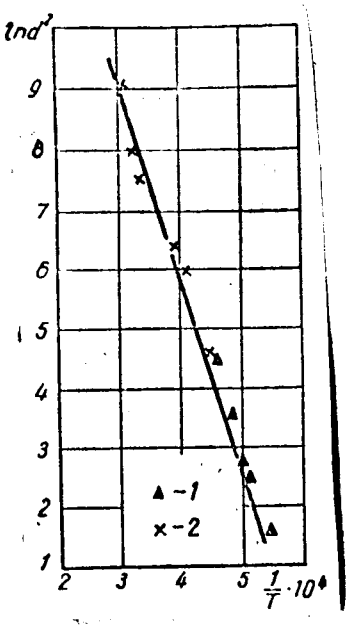

Figure 2. Variation in the grain size of $NbC_{0.80}$. $\ln d^2 = f(\frac{1}{T})$ as a function of temperature: 1- experiments in the vacuum, 2- experiments in argon.

CONCLUSIONS

The temperature dependence of grain size in a nonstoichiometric niobium carbide $NbC_{0.80}$ was investigated in the temperature range of 1600-3300°K. The activation energy for the grain-growth process has been determined as 65.5 kcal/mole. This value makes it possible for us to assume that the process is controlled by boundary and surface diffusion.

REFERENCES

1. Samsonov, G. V. and Portnoy, K. I. Splavy na osnove tugoplankikh soyedineniy (Alloys Based on High Temperature Compounds) Oborongiz, Moscow, 1961.
2. Bauman, M. Sb. "Preobrazovaniye tepla i khimicheskoy energii v elektroenergiyu v raketnykh sistemakh" (IN: "The Transformation of Heat and Chemical Energy into Electrical Energy in Rocket Systems"), IL, Moscow, 118, 1963.
3. Hoch, M., Blackburn, P. E., Dingledy, D. P. and Jonston, H. L. J. Phys. Chem., 59, No. 2, 97, 1955.
4. Chupka, W. A., Berkovitz, I., Giese, C. A. and Inghram, M. G. J. Phys. Chem., 62, No. 5, 611, 1958.
5. Kempter, C. P., Nadler, M. R. J. Chem. Phys., 32, No. 5, 1477, 1960.
6. Frics, R. I. J.Chem. Phys., 37, 320, 1962.
7. Avarbe, R. G. Poroshkovaya metallurgiya (Powder Metallurgy), No. 1, 1965.
8. Avarbe, R. G. and Nikol'skiy, S. S. Teplofizika vysokikh temperatur (The Physics of Heat at High Temperatures), No. 1, 39, 1963.

9. Avarbe, R. G. and Vil'k, Yu. N. Teplofizika vysokikh temperatur (The Physics of Heat at High Temperatures), No. 3, 1106, 1964.
10. Deryagin, B. V. Opredeleniye udel'noy poverkhnosti poroshkoobraznykh tel po soprotivleniyu fil'tratsii razrezhennogo vozdukha (Determining the Specific Surface area of Powder-Like Bodies from the Filtration Resistance of Rarefied Air), Izd-vo AN SSSR, 1957.
11. Ordan'yan, S. S., Avgustinik, A. I. and Vigdergauz, V. Sh. Issledovaniya v oblasti khimii silikatov (Investigations on the Chemistry of Silicates), Collected Works, No. 4, Izd-vo "Nauka," 1965.
12. Blanter, M. Ye. Metodika issledovaniya metallov i obrabotka opytnykh dannykh (Procedures for Investigating Metals and Processing Experimental Data), Metallurgizdat, 271, 1952.
13. Van Buren Defekty v kristallakh (Defects in Crystals), Inostrannaya Literatura (IL), Moscow, 377, 1962.
14. Gel'd, P. and Lyubimov, V. D. "Metallurgiya i toplivo", Izv. AN SSSR, OTN, 119, 1961.

Translated for the National Aeronautics and Space Administration
by John F. Holman and Co. Inc.
WASHINGTON, D. C. 20037
NASw-1495